OPTICAL FIBER METHODS FOR AUTOCLAVE AND EPOXY CURE MONITORING

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INTRODUCTION

The fabrication process of recently developed advanced technology hybrid structures has placed a demand on methods to monitor the state of cure of resins and epoxies commonly used in composite materials. Such monitoring allows in-situ process control insuring homogeneous structural integrity. Furthermore, fabrication costs can be reduced by avoiding the need to "over cure" the composite specimens. Existing techniques such as differential scanning calorimetry (DSC), optical spectroscopy, and dielectric spectroscopy lack the in-situ capabilities required to monitor localized cure state. Other methods, including ultrasonic wave monitoring, are absolute in nature, require frequent calibration, and involve complex measurement systems for monitoring localized cure state [1-3]. We propose to expand upon a principle recently suggested by M. A. Afromowitz, in which optical waveguides made out of the hybrid resin material itself are embedded within the specimen to be monitored [4]. Such implementation exploits some of the advantages of fiber optic sensing techniques, while avoiding the incorporation of "foreign materials" which might cause inhomogeneities in the composite structure.

BACKGROUND

Principle of Refractive Index Change

Afromowitz suggested to take advantage of the fact that the refractive index of a resin might change by as much as 1 % as it cures. An optical waveguide may be fabricated using such resins as the fiber core material. When a cured resin fiber is embedded in a composite structure the uncured resin serves as a waveguide cladding, allowing for the propagation of an optical signal. Ideally, as the resin of the composite structure reaches the cured state, its index will approach that of the embedded resin fiber causing a decrease in transmitted optical power and, eventually, a blend of the fiber into the surrounding composite material.

Waveguide Mode Number Theory

By focusing on the simplest case, the transmissive, step index fiber mode, it is possible to correlate the change in transmitted optical power to the change in cure time. The number of "optical modes" in the step index waveguide can be approximated by

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$$M = \frac{V^2}{2} \quad , \tag{1}$$

where V, the waveguide normalized frequency, is given by

$$V = \frac{2\pi a}{\lambda}(n_1^2 - n_2^2)^{1/2} \quad . \tag{2}$$

In Equation 2, "a" represents the radius of the waveguide core, λ is the operating wavelength, and n_1 and n_2 are the refractive indexes of the waveguide core and cladding, respectively. The change in transmitted power with respect to cure time, dP/dt, is given by

$$\frac{dP}{dt} = \frac{dP}{dn_2}\frac{dn_2}{dt} \quad , \tag{3}$$

where dP/dn_2 is assumed to be proportional to dM/dn_2, that is

$$\frac{dP}{dn_2} = K\frac{dM}{dn_2} \quad . \tag{4}$$

K depends on several factors, including launch conditions and implementation mode (transmissive, reflective, or reentrant loop). K can be made large, for example, by using a higher order mode launch or by increasing the resin fiber interaction length. Both techniques are discussed in the experimental section of this paper.

EXPERIMENTS/RESULTS

Resin Spectral Response

Resin spectral measurements were required to find the optimum operating wavelength for sensor use. For the Biphenol-A-Diglycidylether resin used in this study attenuation was lowest in the 600 to 1100 nm range, with a relative minimum at approximately 1300 nm (see Figure 1). This allowed for subsequent experiments to be conducted at either 633 nm (transmissive mode) or 904 nm (reflective mode) with relatively low resin fiber losses (< 1 dB/cm).

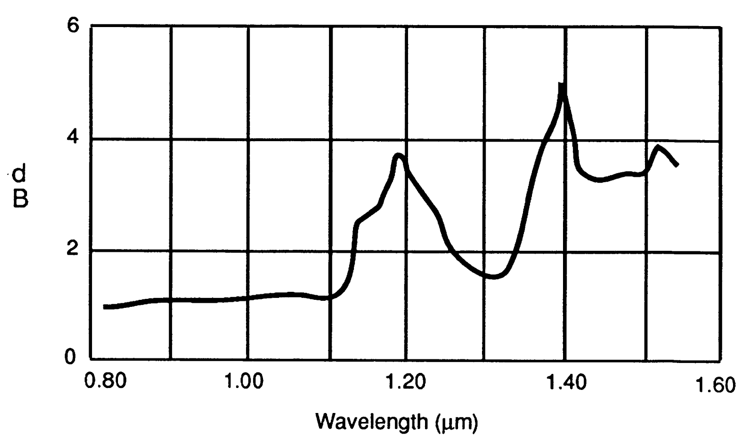

Figure 1. Spectral Attenuation Graph for the Biphenol-Diglycidylether Resin Used in the Experiments.

The Transmissive Mode Cure Monitor

The transmissive mode cure monitor was used to a) confirm results obtained by Afromowitz, and b) investigate the effects of varying the length of the resin fiber. The epoxy used consisted of a fast cure Biphenol-A-Diglycidylether resin, of which three different fiber lengths (4.2, 8.4, 12.6 cm) were drawn manually just prior to gel point. A schematic of the experiment set-up is shown in Figure 2. Large core, 200/230 μm hard clad silica (HCS) fiber was used to access the resin fiber. Figure 3 shows how normalized transmitted power varies as a function of cure time and resin fiber interaction length. Based on these results it can be concluded that the sensitivity, $|dP/dt|$ is highly dependent on the length of the monitoring fiber. This is to be expected, since more "modes" are allowed to interact with the resin in the longer fibers. However, $|dP/dt|$ cannot be increased over the entire cure process by increasing resin fiber interaction length due to a significant loss of information on the cure state during the latter part of the cure. This is seen from the fact that the normalized transmitted power levels off at approximately 3 minutes into the cure for the 12.6 cm case.

Comparison to Spectroscopic Methods

An epoxy cure kinetic study was performed using infrared spectroscopic methods to verify the performance of the proposed sensor. Optical absorption was monitored across the wavenumber range of 4000 - 700 cm^{-1}. The kinetic rate of cure was determined by monitoring an absorption band at 830 cm^{-1} (epoxy ring vibration) normalized for film thickness by ratio to the absorption band at 1610 cm^{-1}. Cure was monitored from the time of casting to 20 minutes. The operation of the proposed fiber optic cure monitor was verified by comparing the slopes of the three curves shown in Figure 3 to the slope of the epoxy cure kinetic curve (Figure 4: Normalized Peak

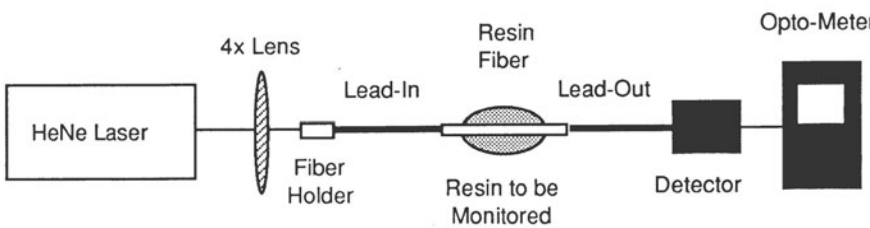

Figure 2. Transmissive Mode Epoxy Cure Monitoring Set-Up.

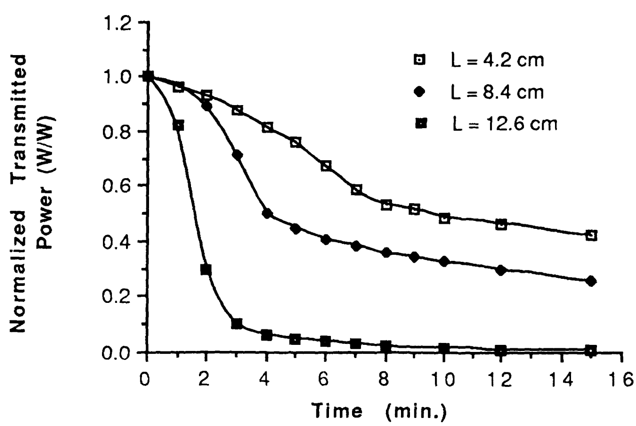

Figure 3. Graph Showing Normalized Transmitted Power Versus Cure Time for Various Resin Fiber Interaction Lengths.

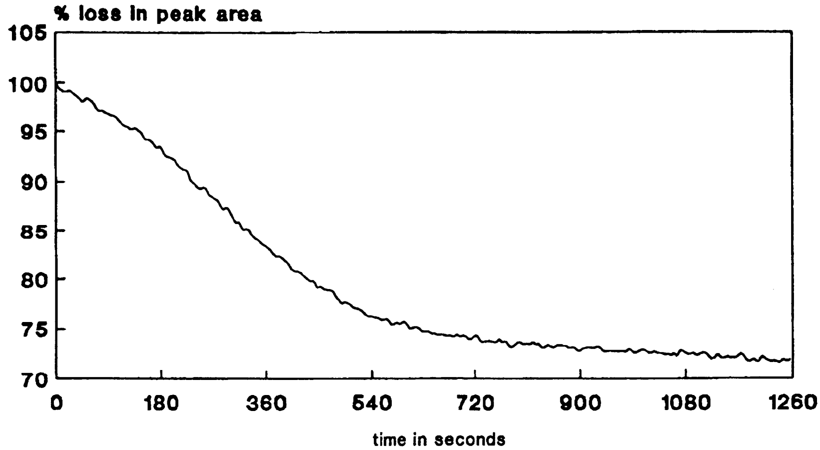

Figure 4. Graph Showing Normalized Peak Absorbance Versus Epoxy Cure Time.

Absorbance Versus Epoxy Cure Time) in their respective linear ranges. After normalizing the slopes of the curves shown in Figure 3 to their respective fiber lengths, they coincided with the slope of the curve shown in Figure 4.

The Reflective Mode Cure Monitor

One objective of this study was to investigate the feasibility of performing the cure monitoring process in the reflective mode, i. e., single end access to the resin fiber. In addition to reducing the complexity of the monitoring system, the reflective mode provides means to double the resin fiber interaction length. This might be beneficial for small structure measurements where sensitivity needs to be improved by increasing the interaction length. The experiment (see Figure 5) was implemented by using a pulsed laser operating at 904 nm, launching its signal through a beam splitter into a 200/230 μm HCS lead fiber, which coupled its output into a 7 cm long resin fiber. At the far end of the resin fiber, a mirror was used to increase the intensity of the reflected signal, which was directed through the beam splitter onto a GaAs APD photodetector. The output of the photodetector was sampled and displayed on an oscilloscope. As shown in Figure 6, the reflected pulse intensity dropped from a peak level of approximately 35 mV (t = 0 min.) to an equilibrium level of approximately 5 mV (t = 3.5 min.) as the cure progressed (0.5 min. intervals).

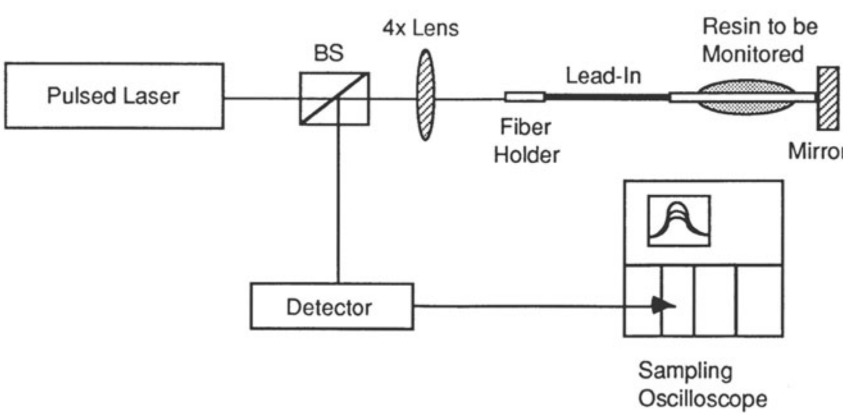

Figure 5. Reflective Mode Epoxy Cure Monitoring Set-Up Using a 904 nm Pulsed Laser.

Higher Order Mode Launch Approach

Earlier it was mentioned that sensitivity might be improved (i. e., K increased) by selectively exciting the higher order optical modes in the resin fiber. This can be achieved by positioning the lead fiber at an angle relative to the axis of the resin fiber. In our experiments a launch angle of approximately 15° was used to verify the sensitivity improvement approach. Figure 7 shows a graph of normalized transmitted power versus cure time for a launch angle of 0° and 15° , respectively (4.2 cm interaction length). As is evident from this graph, an improvement in $|dP/dt|$ from $t = 0$ to $t = 9$ min. has been achieved. Notice that in both cases the point at which $|dP/dt|$ falls below an arbitrary threshold limit remains the same, indicating that sensitivity has been improved throughout the cure process. It is also important to point out that these types of results are extremely repeatable, inspiring confidence in this approach.

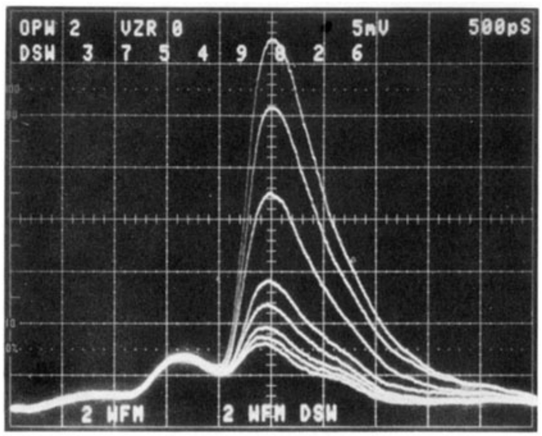

Figure 6. Oscilloscope Trace of the Reflected Cure Monitor Pulse (0.5 Min. Intervals).

DISCUSSION

It was shown that several modifications to the basic fiber optic cure monitor can be used to achieve different goals. Single end access, operating wavelength, resin fiber length, and launch conditions all need to be considered for different types of applications. In particular, we anticipate the need for monitoring techniques applicable to small structures. In such instances it is important to increase the interaction length to achieve desired sensitivity. In many cases it is expected that the reflective mode approach, with the capability of doubling the interaction length, will not yield sufficient sensitivity. It is thus proposed to investigate the performance of fiber optic reentrant loops, which allow multiple recirculations through the resin fiber. In fact, it was demonstrated that pulse recirculation numbers in excess of 6 have been possible with short length (2 cm) resin fibers. Such performance is anticipated to make cure monitoring on structures less than 5 mm in length feasible.

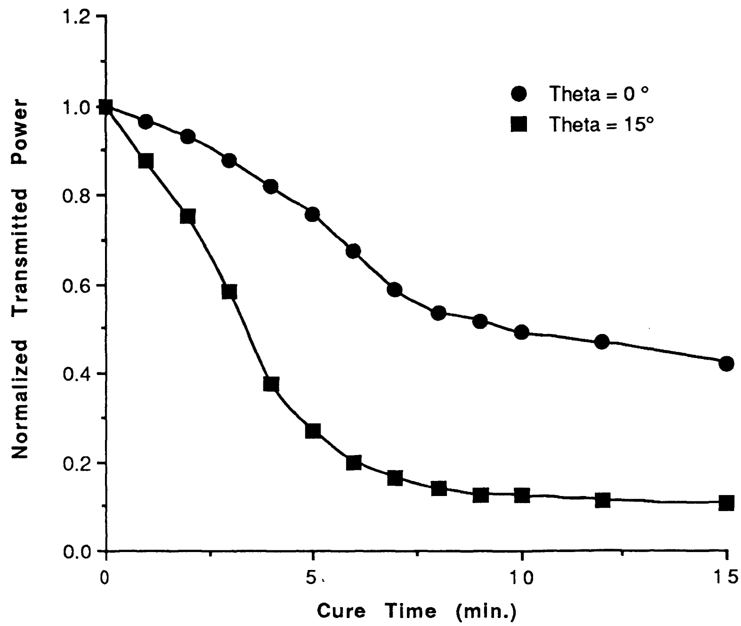

Figure 7. Plot of Normalized Transmitted Power Versus Cure Time Showing the Effects of a Higher Order Mode Launch.

CONCLUSIONS

It has been demonstrated that optical fiber methods may allow cure monitoring of epoxies and resins used in the fabrication of composite structures. Three modes of operation were analyzed: transmission, reflection, and higher order mode launch. From the transmissive mode experiments it was determined that a maximum resin fiber length exists beyond which sensitivity is sacrificed during the latter parts of the cure. Single end access measurements have been achieved in the reflective mode, reducing the complexity of the monitoring system. Higher order mode launch techniques have allowed improvements in |dP/dt| over the entire cure process. The results of the fiber optic cure monitor were verified by IR spectroscopic methods. Future work includes the study of fiber optic reentrant loops to increase the resin interaction length.

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